Solvatochromic Parameters for Near-Critical Water

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As an environmentally benign replacement of hazardous organic solvents, nearcritical water (liquid water in the temperature range of 200 to 300°C) solubilizes organics as well as ionics, and also can act as a source of hydronium and hydroxide due to its higher ionization constant in comparison with ambient water. Nearcritical water has been used successfully for chemical reactions including base- and acid-catalyzed reactions and has drawn intensified interest for more potential applications. Although a knowledge of the solvent properties for nearcritical water is crucial for understanding and designing physicochemical processes, current data are limited.

We have chosen a series of solvatochromic probes sufficiently stable for use in high-temperature water, and have constructed a spectroscopic apparatus to investigate the solvatochromic behavior of these probes in nearcritical water. The apparatus provides for rapid heating and measurements to minimize the effect of hydrolysis of the probe molecules. We report experimental measurements of the dipolarity/polarizability scale π^*, the hydrogen-bonding donor scale α, and the hydrogen-bonding acceptor scale β for water at saturation at 25 - 275°C. The solvent parameters are strongly temperature dependent, as would be expected considering the wide variation in properties over this range. Based on the well-established linear solvation energy relationship (LSER) of Kamlet and Taft, those solvent scales are used for correlating the solubilities, phase equilibria and limiting activity coefficients in nearcritical water, as might be used in the design of commercial processes.